

{[Bis(dimethylamino)boryl]methyl} dimethylphosphane as ligand in transition metal complexes

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Received 19 February 1997; received in revised form 30 April 1997

Abstract

The new α,ω -[phosphanyl(organyl)]borane $\text{Me}_2\text{PCH}_2\text{B}(\text{NMe}_2)_2$ (**8**) was obtained in good yield by the reaction of $\text{ClB}(\text{NMe}_2)_2$ with $\text{LiCH}_2\text{PMe}_2$. Compound **8** forms the transition metal complexes $[(\text{CO})_5\text{Cr}(\text{Me}_2\text{PCH}_2\text{B}(\text{NMe}_2)_2)]$ (**9**), $[(\text{MeC}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{Me}_2\text{PCH}_2\text{B}(\text{NMe}_2)_2)]$ (**10**), and $[(\text{CO})_4\text{Fe}(\text{Me}_2\text{PCH}_2\text{B}(\text{NMe}_2)_2)]$ (**11**), which were isolated as highly volatile liquids in high yields. Complex **11** easily underwent exchange reactions of the Me_2N substituents which led to derivatives with threefold coordinated boron such as $[(\text{CO})_4\text{Fe}(\text{Me}_2\text{PCH}_2\text{B}(\text{OMe})_2)]$ (**13**), and $[(\text{CO})_4\text{Fe}(\text{Me}_2\text{PCH}_2\text{B}(\text{NMe}_2)\text{Cl})]$ (**14**), or to a compound with tetrafold coordinated boron, $[(\text{CO})_4\text{Fe}(\text{Me}_2\text{PCH}_2\text{BCl}_2(\text{NHMe}_2))]$ (**15**). $\text{Li}[(\text{CO})_4\text{Fe}(\text{Me}_2\text{PCH}_2\text{BH}_3)]$ (**16**), *cis,trans*- $[(\text{CO})_4\text{Fe}(\text{Me}_2\text{PCH}_2\text{BH}_2)_2]$ (**17**), and $[(\text{CO})_4\text{Fe}(\text{Me}_2\text{PCH}_2\text{BH}_2(2,4,6\text{-Me}_3\text{C}_5\text{H}_2\text{N}))]$ (**18**) were obtained from **13** by corresponding substitution of the MeO groups. The addition of HSiPh_3 to the iron center was achieved by photolysis of **13**, giving $[(\text{CO})_3\text{FeH}(\text{SiPh}_3)(\text{Me}_2\text{PCH}_2\text{B}(\text{OMe})_2)]$ (**19**). $[(\text{CO})_5\text{Cr}(\text{Me}_2\text{PCH}_2\text{B}(\text{OMe})_2)]$ (**12**), the chromium analogue of **13**, was obtained from the reaction of $[(\text{CO})_5\text{Cr}(\text{Me}_2\text{PCH}_2\text{B}(\text{NMe}_2)_2)]$ (**9**) with MeOH. The structure of compound **19** was determined by single crystal X-ray diffraction. © 1997 Elsevier Science S.A.

1. Introduction

Only few α,ω -[phosphanyl(organyl)]boranes of the type $\text{R}_2\text{P}(\text{CR}'_x)_n\text{BR}'_2$ were reported till now. Examples include $\text{Et}_2\text{P}(\text{CH}_2)_2\text{B}[\text{O}_2(\text{CH}_2)_2]$ (**1**) [1] and the dimeric $(\text{Me}_2\text{PCH}_2\text{BMe}_2)_2$ (**2**) [2], both showing a saturated organic bridge between boron and phosphorus, and the ethylene bridged compounds $\text{Me}_2\text{PCMe}=\text{CMeBMe}_2$ (**3**) [3] and *E*- $\text{Ph}_2\text{PCH}=\text{CHBMe}_2$ ($\text{Me} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$) (**4**) [4]. An α,ω -[phosphanyl(organyl)]borane with an aromatic spacer between phosphorus and boron was obtained from the reaction of LiPMe_2 with BBr_3 , which gave not the borylphosphane Me_2PBBR_2 (**5a**), but led to $\text{Me}_2\text{P}[\text{2}-(\text{Br}_2\text{BCH}_2)_4,6\text{-Me}_2\text{C}_6\text{H}_2]$ (**5b**) by 1,2-addition of one CH moiety of an *o*-Me group to the phosphorus–boron double bond in the intermediate **5a** [5]. The compound *o*- $\text{Ph}_2\text{PCH}_2\text{C}_6\text{H}_4\text{BtBu}_2$ (**6**) [6] exhibits a similar organic backbone, but now with phosphorus in the benzyl position. Generally, these compounds show inter- or intramolecular formation of bonds between phosphorus

and the electron-deficient boron. Exceptions, because of electronic or steric reasons, are compounds **1** and **4**, respectively (Fig. 1).

The chemistry of α,ω -[phosphanyl(organyl)]silanes as bidentate ligands in transition metal complexes is well established [7,8]. Especially the chelate assisted hydrosilylation gives access to a large number of new transition metal silyl complexes. Due to the diagonal relationship between silicon and boron, a similar reactivity for the corresponding α,ω -[phosphanyl(organyl)]boranes might be expected. Information about these compounds as ligands to transition metals, however, is restricted to $[\text{Rh}(\text{CO})\text{Cl}\{\text{Me}_2\text{P}(\text{CMe})_2\text{BMe}_2\}_2]$ (**7**) [9] as the only example, which was obtained by the reaction of **3** with $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$. On the basis of IR and ^{31}P NMR spectra, a dative bond from the rhodium center to boron was suggested, but it was not possible to support this assumption by ^{11}B NMR or structural data.

We have started to investigate the properties of suitable α,ω -[phosphanyl(organyl)]boranes as ligands in transition metal complexes, since the possible formation of an intramolecular metal–boron bond, which might be favored by chelating assistance, is of special interest.

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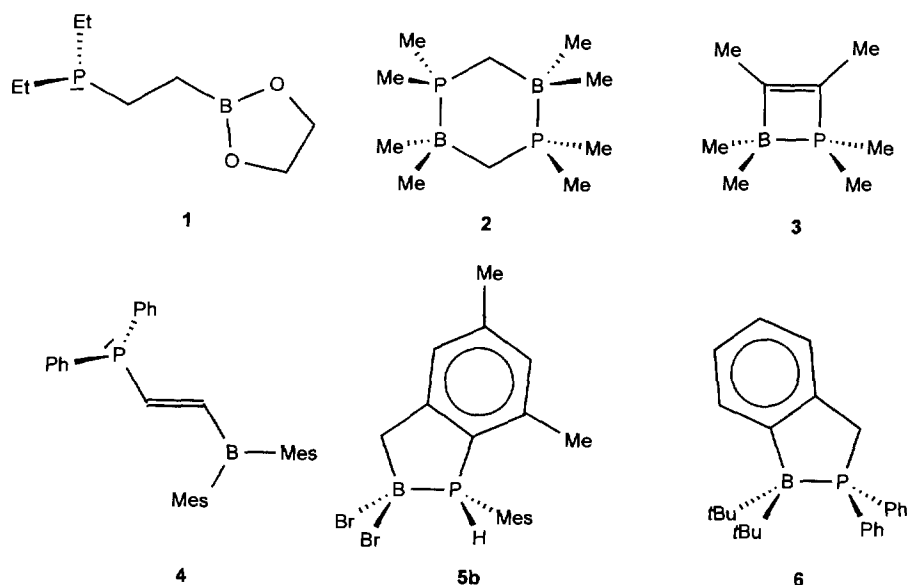


Fig. 1.

Thus far, stable complexes with two center–two electron bonds between the transition metal and boron are known mainly for the catecholboranyl ligand [10–21] (Cat = 1,2-O₂C₆H₄) and for some diborane(4)yl [22] and borylene [23] ligands. The oxidative addition of a boron–hydrogen or boron–boron bond, respectively, to the metal center already led to several boryl complexes of early [15], middle [20–22] and late [11,12,16] transition metals, hence, the intended intramolecular formation of a metal–boron bond may be achieved in a similar manner. A suitable ligand for this purpose should provide a threefold coordinated phosphorus atom to coordinate at the metal center, and reactive groups at the boron atom.

This paper describes the synthesis and characterization of Me₂PCH₂B(NMe₂)₂ (**8**), which was chosen as a model ligand for our investigations, and first results about the reactivity of **8** towards various transition metal complexes.

2. Experimental section

2.1. General considerations

All manipulations were carried out by standard Schlenk techniques under N₂. PMe₃ was a generous gift from Hoechst, Knapsack. All other reagents were purchased from commercial suppliers and used without further purification. Solvents and deuterated solvents for NMR experiments were dried and purified by standard methods. [MeC₅H₄Mn(CO)₂(THF)] [24], [(CO)₅Cr(THF)] [25], LiCH₂PMe₂ [26], and ClB(NMe₂)₂ [27] were prepared by literature procedures. A Heraeus TQ 150 high pressure mercury lamp was used for the irradiation.

2.2. Spectroscopic studies

¹H, ¹¹B, ¹³C, and ³¹P NMR data were obtained on a Varian Unity 500 in CDCl₃ as solvent with TMS as internal, and BF₃ · OEt₂, and H₃PO₄ (85%) as external standards. IR spectra were recorded on a Perkin–Elmer FTIR 1720 X spectrometer in CHCl₃ solutions. Mass spectra were recorded on a Finnigan MAT 95 (70 eV) and elemental analyses (C, H, N) were obtained from a Carlo–Erba elemental analyzer, Model 1106.

2.3. Synthesis of Me₂PCH₂B(NMe₂)₂ (**8**)

A solution of 4.95 g (36.94 mmol) (Me₂N)₂BCl in 50 ml of hexane was added dropwise to 3.03 g (36.94 mmol) LiCH₂PMe₂ dissolved in 100 ml of THF, at –78°C. The reaction mixture was warmed up to room temperature and stirred for 16 h. After removal of the solvent, the pure compound was distilled at 4 Torr and 55°C as a colorless oil. Yield: 4.10 g, 70%. ¹H NMR: δ 0.95 (d, ²J_{PH} = 3.05 Hz, 2H, PCH₂B), 1.03 (d, ²J_{PH} = 2.37 Hz, 6H, PCH₃), 2.66 (s, 12H, NCH₃). ¹¹B NMR: δ_B 31.05. ¹³C NMR: δ 16.69 (d, ¹J_{PC} = 13.5 Hz, PCH₃), 18.30 (br, PCH₂B), 40.5 (s, NCH₃). ³¹P NMR: δ_P –48.8. MS *m/z* (relative intensity) = 174 (34%, M⁺), 130 (7%, M⁺–NMe₂), 111 (28%, M⁺–PMe₂), 100 (100%, M⁺–CH₂PMe₂), 56 (40%, M⁺–CH₂PMe₂–NMe₂), 44 (73%, NMe₂). Anal. Calcd. for C₇H₂₀BN₂P (174.04): C, 48.31; H, 11.58; N, 16.10. Found: C, 48.37; H, 11.72; N, 15.44.

2.4. Synthesis of [(CO)₅Cr(Me₂PCH₂B(NMe₂)₂)] (**9**)

A solution of 1.20 g (5.45 mmol) [Cr(CO)₆] in 100 ml of THF was irradiated at room temperature for 4 h.

To the resulting mixture, 0.95 g (5.45 mmol) of **8** were added. After stirring for 16 h, the solvent was removed and the pure compound was distilled at 10^{-4} Torr and 130°C as a colorless oil. Yield: 1.40 g, 70%. ^1H NMR: δ 1.44 (d, $^2J_{\text{PH}} = 7.63$ Hz, 6H, PCH_3), 1.46 (d, $^2J_{\text{PH}} = 9.16$ Hz, 2H, PCH_2B), 2.64 (s, 12H, NCH_3). ^{11}B NMR: δ_{B} 32.67. ^{13}C NMR: δ 19.22 (d, $^1J_{\text{PC}} = 25.0$ Hz, PCH_3), 20.00 (br, PCH_2B), 40.70 (s, NCH_3) 217.69 (d, $^2J_{\text{PC}} = 14.0$ Hz, 4C, CrCO_{eq}), 222.11 (d, $^2J_{\text{PC}} = 8.03$ Hz, 1C, CrCO_{ax}). ^{31}P NMR: δ_{P} 16.81. IR: 2060.7(s), 1976.3(w), 1931.1(vs). MS m/z (relative intensity) = 282 (1%, $\text{M}^+ - 3\text{CO}$), 286 (7%, $\text{M}^+ - \text{B}(\text{NMe}_2)_2$), 240 (1%, $\text{M}^+ - \text{B}(\text{NMe}_2)_2 - \text{CO}$), 210 (18%, $\text{M}^+ - \text{B}(\text{NMe}_2)_2 - 2\text{CO} - 2\text{H}$), 184 (4%, $\text{M}^+ - \text{B}(\text{NMe}_2)_2 - 3\text{CO}$), 156 (8%, $\text{M}^+ - \text{B}(\text{NMe}_2)_2 - 4\text{CO}$), 128 (29%, $\text{M}^+ - \text{B}(\text{NMe}_2)_2 - 5\text{CO}$), 77 (10%, PMe_3), 44 (18%, NMe_2). Anal. Calcd. for $\text{C}_{12}\text{H}_{20}\text{BN}_2\text{O}_3\text{PCr}$ (366.08): C, 39.37; H, 5.51; N, 7.65. Found: C, 39.14; H, 5.90; N, 8.08.

2.5. Synthesis of $[(\text{MeC}_5\text{H}_4)\text{Mn}(\text{CO})_2\{\text{Me}_2\text{PCH}_2\text{B}(\text{NMe}_2)_2\}]$ (**10**)

A solution of 1.18 g (5.40 mmol) $[(\text{MeC}_5\text{H}_4)\text{Mn}(\text{CO})_3]$ in 100 ml of THF was irradiated at room temperature for 4 h, subsequently, 0.94 g (5.40 mmol) **8** were added to the dark red reaction mixture which was stirred for 16 h. A gradual lightening was observed until the solution became yellow. After removal of the solvent, the product was distilled at 10^{-4} Torr and 120°C as a yellow oil. Yield: 1.73 g, 88%. ^1H NMR: δ 1.35 (br, 6H, PCH_3), 1.92 (s, 3H, CpCH_3), 2.20 (br, 2H, PCH_2B), 2.65 (s, 12H, NCH_3), 4.28 (d, $^3J_{\text{PH}} = 18.01$ C₅H₄). ^{11}B NMR: δ_{B} 31.03. ^{13}C NMR: δ 14.07 (s, CpCH_3), 21.68 (d, $^1J_{\text{PC}} = 27.4$ Hz, PCH_3), 22.00 (br, PCH_2B), 40.74 (s, NCH_3), 81.97, 82.30, 98.19 (C₅H₄) 233.12 (CO). ^{31}P NMR: δ_{P} 57.18. IR: 1931.9(s), 1845.1(s). MS m/z (relative intensity) = 364 (3%, M^+), 308 (2%, $\text{M}^+ - 2\text{CO}$), 288 (1%, $\text{M}^+ - \text{MeC}_5\text{H}_4$), 229 (3%, $\text{M}^+ - 2\text{CO} - \text{MeC}_5\text{H}_4$), 190 (8%, $\text{M}^+ - \text{Me}_2\text{PCH}_2\text{B}(\text{NMe}_2)_2$), 162 (25%, $\text{M}^+ - \text{Me}_2\text{PCH}_2\text{B}(\text{NMe}_2)_2 - \text{CO}$), 134 (100%, MnMeC_5H_4), 99 (7%, $\text{B}(\text{NMe}_2)_2$), 79 (30%, MeC_5H_4), 55 (32%, Mn). Anal. Calcd. for $\text{C}_{15}\text{H}_{27}\text{BN}_2\text{O}_2\text{PMn}$ (364.12): C, 49.48; H, 7.47; N, 7.69. Found: C, 49.26; H, 7.18; N, 7.33.

2.6. Synthesis of $[(\text{CO})_4\text{Fe}\{\text{Me}_2\text{PCH}_2\text{B}(\text{NMe}_2)_2\}]$ (**11**)

To a suspension of 2.78 g (7.65 mmol) $[\text{Fe}_2(\text{CO})_9]$ in 50 ml of THF 1.33 g (7.65 mmol) **8** were added and the reaction mixture was stirred for 24 h at room temperature. Meanwhile, the suspension cleared up and turned to a dark red color. After removal of the volatiles in high vacuum, the residue was extracted with 50 ml of hexane and filtered. Again, the volatiles were pumped

off and the product was distilled at 10^{-4} Torr and 140°C as a yellow oil. Yield: 2.09 g, 80%. ^1H NMR: δ 1.60 (d, $^2J_{\text{PH}} = 10.07$ Hz, 6H, PCH_3), 1.64 (d, $^2J_{\text{PH}} = 14.04$ Hz, 2H, PCH_2B), 2.67 (s, 12H, NCH_3). ^{11}B NMR: δ_{B} 31.50. ^{13}C NMR: δ 20.62 (d, $^1J_{\text{PC}} = 32.9$ Hz, PCH_3), 21.81 (br, PCH_2B), 40.74 (s, NCH_3) 214.32 (d, $^2J_{\text{PC}} = 20.3$ Hz, FeCO). ^{31}P NMR: δ_{P} 44.16. IR: 2046.0(m), 1968.3(w), 1931.2(s). MS m/z (relative intensity) = 342 (24%, M^+), 302 (48%, $\text{M}^+ - \text{NMe}_2$), 243 (33%, $\text{M}^+ - \text{B}(\text{NMe}_2)_2$), 167 (19%, $\text{Fe}(\text{CO})_4$), 131 (62%, Me_2PFe), 99 (10%, $\text{B}(\text{NMe}_2)_2$), 76 (83%, PMe_3), 57 (41%, Fe), 44 (32%, NMe_2). Anal. Calcd. for $\text{C}_{11}\text{H}_{20}\text{BN}_2\text{O}_4\text{PFe}$ (341.92): C, 38.64; H, 5.90; N, 8.19. Found: C, 38.21; H, 6.13; N, 8.31.

2.7. Synthesis of $[(\text{CO})_5\text{Cr}\{\text{Me}_2\text{PCH}_2\text{B}(\text{OMe})_2\}]$ (**12**)

A total of 5 ml of MeOH was added to a solution of 1.98 g (5.40 mmol) **9** in 50 ml of toluene at 0°C . The mixture was warmed up to room temperature, stirred for 3 h, and filtered. All volatiles were removed in high vacuum and the product was distilled at 10^{-4} Torr and 110°C as a colorless liquid. Yield: 1.31 g (71.3%). ^1H NMR: δ 0.70 (d, $^2J_{\text{PH}} = 11.30$ Hz, 2H, PCH_2B), 1.07 (d, $^2J_{\text{PH}} = 7.94$ Hz, 6H, PCH_3), 3.23 (s, 6H, BOCH_3). ^{11}B NMR: δ_{B} 29.20. ^{13}C NMR: δ 18.01 (br, PCH_2B), 20.03 (d, $^1J_{\text{PC}} = 25.2$ Hz, PCH_3), 51.27 (s, OCH_3), 217.83 (d, $^2J_{\text{PC}} = 14.2$ Hz, CrCO_{eq}), 222.13 (d, $^2J_{\text{PC}} = 8.8$ Hz, CrCO_{ax}). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ_{P} 12.45. IR: 2059(m), 1974(w), 1931(s). MS: m/z (relative intensity) = 340 (12%, M^+), 312 (1%, $\text{M}^+ - \text{CO}$), 284 (1%, $\text{M}^+ - 2\text{CO}$), 256 (2%, $\text{M}^+ - 3\text{CO}$), 228 (20%, $\text{M}^+ - 4\text{CO}$), 200 (100%, $\text{M}^+ - 5\text{CO}$), 148 (3%, $\text{M}^+ - \text{Cr}(\text{CO})_5$). Anal. Calcd. for $\text{C}_{10}\text{H}_{14}\text{BO}_7\text{PCr}$ (340.00): C, 35.33; H, 4.15. Found: C, 34.96; H, 4.19.

2.8. Synthesis of $[(\text{CO})_4\text{Fe}\{\text{Me}_2\text{PCH}_2\text{B}(\text{OMe})_2\}]$ (**13**)

A total of 5 ml of MeOH was added to a solution of 3.89 g (11.40 mmol) **11** in 50 ml of toluene at 0°C . The mixture was warmed up to room temperature, stirred for 3 h, and filtered. All volatiles were removed in high vacuum, and the product was distilled at 10^{-4} Torr and 100°C as a yellow liquid. Yield: 2.64 g (73.3%). ^1H NMR: δ 1.52 (d, $^2J_{\text{PH}} = 14.25$ Hz, 2H, PCH_2B), 1.70 (d, $^2J_{\text{PH}} = 10.18$ Hz, 6H, PCH_3), 3.61 (s, 6H, BOCH_3). ^{11}B NMR: δ_{B} 28.00. ^{13}C NMR: δ 18.82 (br, PCH_2B), 21.46 (d, $^1J_{\text{PC}} = 32.9$ Hz, PCH_3), 51.90 (s, OCH_3), 213.83 (d, $^2J_{\text{PC}} = 20.3$ Hz, FeCO). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ_{P} 44.16. IR: 2046(m), 1968(s), 1931(s). MS: m/z (relative intensity) = 315 (1%, M^+), 287 (10%, $\text{M}^+ - \text{CO}$), 259 (9%, $\text{M}^+ - 2\text{CO}$), 232 (30%, $\text{M}^+ - 3\text{CO}$), 204 (100%, $\text{M}^+ - 4\text{CO}$), 132 (7%, $\text{M}^+ - 4\text{CO} - \text{B}(\text{OMe})_2$), 73 (3%, $\text{B}(\text{OMe})_2$). Anal. Calcd. for $\text{C}_9\text{H}_{14}\text{BO}_6\text{PFe}$ (315.84): C, 34.23; H, 4.47. Found: C, 33.88; H, 4.01.

2.9. Synthesis of $[(CO)_4Fe(Me_2PCH_2B(NMe_2)Cl)]$ (**14**)

A solution of 0.21 g (1.75 mmol) of BCl_3 in 0.67 ml of hexane was added to a solution of 0.60 g (1.75 mmol) **11** in 30 ml of toluene at 0°C. The mixture was warmed up to room temperature, stirred for 1 h, and filtered. From the filtrate, all volatiles were removed in high vacuum and the compound was obtained as a yellow solid. Yield: 0.48 g (82.3%). 1H NMR: δ 1.26 (d, $^2J_{PH} = 10.5$ Hz, 6H, PCH_3), 1.41 (d, $^2J_{PH} = 11.50$ Hz, 2H, PCH_2B), 2.46 (s, 6H, NCH_3). ^{11}B NMR: δ_B 35.12. ^{13}C NMR: δ 21.21 (d, $^1J_{PC} = 31.3$ Hz, PCH_3), 26.50 (br, PCH_2B), 39.50 (s, NCH_3), 214.30 (d, $^1J_{PC} = 20.2$ Hz, $FeCO$). $^{31}P\{^1H\}$ NMR: δ_P 41.28. IR: 2045(m), 1967(w), 1930(s). Anal. Calcd. for $C_9H_{14}BClO_4NPFe$ (333.30): C, 32.43; H, 4.23; N, 4.20. Found: C, 31.97; H, 4.02; N, 4.15.

2.10. Synthesis of $[(CO)_4Fe(Me_2PCH_2BCl_2(NHMe_2))]$ (**15**)

A solution of 0.37 g (10.16 mmol) HCl in 16.66 ml of Et_2O was added to a solution of 0.87 g (2.54 mmol) **11** in 30 ml of toluene at 0°C. The mixture was warmed up to room temperature, stirred for 1 h, concentrated to 15 ml, and filtered. The compound was obtained by removing all volatiles from the filtrate as a white solid. Yield: 0.84 g (89.4%). 1H NMR: δ 1.61 (br, 2H, PCH_2B), 1.79 (br, 6H, PCH_3), 2.81 (s, 6H, NCH_3), 5.63 (s, 1H, NH). ^{11}B NMR: δ_B 7.17. ^{13}C NMR: δ 21.78 (d, $^1J_{PC} = 32.8$ Hz, PCH_3), 30.30 (br, PCH_2B), 39.30 (s, NCH_3), 195.10 (d, $^1J_{PC} = 18.9$ Hz, $FeCO$). $^{31}P\{^1H\}$ NMR: δ_P 36.23. IR: 2045(m), 1965(m), 1927(s). Anal. Calcd. for $C_9H_{15}BCl_2O_4NPFe$ (369.76): C, 29.23; H, 4.09; N, 3.79. Found: C, 28.93; H, 4.59; N, 3.12.

2.11. Synthesis of $Li[(CO)_4Fe(Me_2PCH_2BH_3)]$ (**16**)

A solution of 2.62 g (8.30 mmol) **13** in 15 ml of hexane was added to a suspension of 0.32 g (8.30 mmol) $Li[AlH_4]$ in 40 ml of Et_2O at $-78^\circ C$. The mixture was warmed up to room temperature, stirred for 4 h, and concentrated to 25 ml. A white solid was obtained from this solution at $-30^\circ C$, which was recrystallized from a mixture of 60 ml Et_2O and 30 ml of hexane at $-30^\circ C$. Yield: 1.73 g (79.0%). 1H NMR (all NMR spectra were recorded in C_4D_8O as solvent): δ 0.32 (q, $^1J_{BH} = 85$ Hz, 3H, BH), 0.98 (br, 2H, PCH_2B), 1.53 (d, $^2J_{PH} = 10.37$ Hz, 6H, PCH_3). ^{11}B NMR: δ_B -33.86 (q, $^1J_{BH} = 85$ Hz). ^{13}C NMR: δ 18.36 (d, $^1J_{PC} = 33.5$ Hz, PCH_3), 19.50 (br, PCH_2B), 216.61 (d, $^2J_{PC} = 19.8$ Hz, $FeCO$). $^{31}P\{^1H\}$ NMR: δ_P 43.37. IR (C_4H_8O): ν_{BH} 2237(s), 2082(s); ν_{CO} 2031(m), 1950(w), 1918(s). Anal. Calcd. for $C_7H_{11}BLiO_4PFe$ (263.73): C, 31.88; H, 4.20. Found: C, 31.85; H, 4.05.

2.12. Synthesis of $cis,trans-[(CO)_4Fe(Me_2PCH_2BH_2)]_2$ (**17**)

A solution of 1.95 g (7.40 mmol) **16** in 50 ml of Et_2O was cooled to $-78^\circ C$ and 12.13 ml (7.40 mmol) of a 0.61 M solution of HCl in Et_2O was added dropwise. The mixture was stirred for 2 h, and warmed to room temperature. After removal of all volatiles in high vacuum, the remaining solid was extracted with 50 ml of toluene, and filtered. The compound was isolated as a white precipitate from the filtrate at $-30^\circ C$. Yield: 1.58 g (83.3%). Isomer 1 (70%); $^1H\{^{11}B\}$ NMR: δ 0.40 (br, 2H, μ -BH), 1.01 (d, $^2J_{PH} = 10.00$ Hz, 6H, PCH_3), 1.07 (d, $^2J_{PH} = 14.00$ Hz, 2H, PCH_2B), 3.94 (br, 2H, terminal BH). ^{11}B NMR: δ_B 20.46 (br). ^{13}C NMR: δ_{13} 20.94 (d, $^1J_{PC} = 32.3$ Hz, PCH_3), 21.40 (br, PCH_2B), 214.07 (d, $^2J_{PC} = 20.8$ Hz, $FeCO$). $^{31}P\{^1H\}$ NMR: δ_P 40.42. Isomer 2 (30%); $^1H\{^{11}B\}$ NMR: δ 0.54 (br, 2H, μ -BH), 1.02 (d, $^2J_{PH} = 10.00$ Hz, 6H, PCH_3), 1.09 (d, $^2J_{PH} = 14.00$ Hz, 2H, PCH_2B), 4.03 (br, 2H, terminal BH). ^{11}B NMR: δ_B 20.46 (br). ^{13}C NMR: δ 21.14 (d, $^1J_{PC} = 32.3$ Hz, PCH_3), 21.60 (br, PCH_2B), 213.87 (d, $^2J_{PC} = 20.8$ Hz, $FeCO$). $^{31}P\{^1H\}$ NMR: δ_P 40.59. IR (C_7H_8): $\nu_{BH(i)}$ 2586(w), $\nu_{BH(b)}$ 1605(s); ν_{CO} 2048(m), 1973(w), 1935(s). MS: m/z (relative intensity) = 372 (1%, $M^+ - Fe(CO)_3$), 344 (22%, $M^+ - Fe(CO)_3 - CO$), 316 (18%, $M^+ - Fe(CO)_3 - 2CO$), 288 (75%, $M^+ - Fe(CO)_3 - 3CO$), 260 (100%, $M^+ - Fe(CO)_3 - 4CO$). Anal. Calcd. for $C_{14}H_{20}B_2O_8P_2Fe_2$ (511.57): C, 32.87; H, 3.94. Found: C, 32.57; H, 4.20.

2.13. Synthesis of $[(CO)_4Fe(Me_2PCH_2BH_2(2,4,6-Me_3C_5H_2N))]$ (**18**)

To a solution of 1.02 g (2.00 mmol) **17** in 20 ml of toluene 0.48 g (4.00 mmol) 2,4,6- $Me_3C_5H_2N$ were added at room temperature. The mixture was stirred for 5 h, filtered, and cooled to $-30^\circ C$. The product was obtained as a crystalline, colorless solid. Yield: 1.30 g (86.2%). $^1H\{^{11}B\}$ NMR: δ 1.12 (d/tr, $^2J_{PH} = 12.82$ Hz, $^3J_{HH} = 6.71$ Hz, 2H, PCH_2B), 1.49 (s, 3H, p - CH_3 of 2,4,6- $Me_3C_5H_2N$), 1.65 (d, $^2J_{PH} = 10.38$ Hz, 6H, PCH_3), 2.27 (s, 6H, o - CH_3 of 2,4,6- $Me_3C_5H_2N$), 2.85 (d/tr, 2H, $^3J_{PH} = 6.71$ Hz, $^3J_{HH} = 6.71$ Hz, BH), 5.96 (s, 2H, CH of 2,4,6- $Me_3C_5H_2N$). ^{11}B NMR: δ_B -13.60 (br). ^{13}C NMR: δ 18.82 (br, PCH_2B), 19.32 (d, $^1J_{PC} = 32.9$ Hz, PCH_3), 19.90 (s, p - CH_3 of 2,4,6- $Me_3C_5H_2N$), 23.69 (s, o - CH_3 of 2,4,6- $Me_3C_5H_2N$), 125.94 (s, C2 of 2,4,6- $Me_3C_5H_2NCH_3$), 130.00 (s, C3 of 2,4,6- $Me_3C_5H_2N$), 157.03 (s, C1 of 2,4,6- $Me_3C_5H_2N$), 215.91 (d, $^2J_{PC} = 20.3$ Hz, $FeCO$). $^{31}P\{^1H\}$ NMR: δ_P 42.11. IR: ν_{BH} 2370(w), δ_{BH} 1180(m), ν_{CO} 2040(m), 1962(m), 1923(s). MS: m/z (relative intensity) = 376 (0.5%, $M^+ - H$), 349 (1%, $M^+ - CO$), 321 (3%, $M^+ - 2CO$), 293 (10%, $M^+ - 3CO$), 265 (17%, $M^+ - 4CO$).

Anal. Calcd. for $C_{15}H_{21}BNO_4PFe$ (376.97): C, 47.79; H, 5.62; N, 3.72. Found. C, 47.37; H, 5.53; N, 3.52.

2.14. Synthesis of $[(CO)_3FeH(SiPh_3)(Me_2PCH_2B(OMe)_2)]$ (**19**)

A solution of 3.16 g (10.00 mmol) **13** and 2.61 g (10.00 mmol) $HSiPh_3$ in 250 ml of hexane was irradiated for 3 h at room temperature. The mixture was concentrated to 100 ml and cooled to $-30^\circ C$. After 24 h, the precipitate was collected, and recrystallization from a hexane/toluene mixture (10:1) gave the product as a white solid. Yield: 5.21 g (95.0%). 1H NMR: δ -9.55 (d, $^2J_{PH} = 29.74$ Hz, 1H, FeH), 0.81 (d, $^2J_{PH} = 12.81$ Hz, 2H, PCH_2B), 1.10 (d, $^2J_{PH} = 9.10$ Hz, 6H, PCH_3), 3.23 (s, 6H, $BOCH_3$), 7.25 (br, 9H, *o*- and *p*-H $SiPh_3$), 8.05 (br, 6H, *m*-H $SiPh_3$). ^{11}B NMR: δ_B 28.70. ^{13}C NMR: δ 18.95 (br, PCH_2B), 21.08 (d, $^1J_{PC} = 29.1$ Hz, PCH_3), 51.45 (s, OCH_3), 136.00 (br, *o*-, *m*-, *p*-C $SiPh_3$), 143.00 (s, *ipso*-C $SiPh_3$), 212.44 (d, $^2J_{PC} = 20.3$ Hz, FeCO). $^{31}P\{^1H\}$ NMR: δ_P 18.97. IR: 2035(w), 1980(s), 1963(vs). MS: m/z (relative intensity) = 520 (1%, M^+-CO), 492 (3%, M^+-2CO), 464 (20%, M^+-3CO), 259 (60%, $SiPh_3^+$), 204 (38%, $M^+-3CO-SiPh_3$), 182 (100%, $SiPh_2$). Anal. Calcd. for $C_{26}H_{30}BO_5SiPFe$ (548.24): C, 56.98; H, 5.52. Found: C, 56.58; H, 5.42.

2.15. Synthesis of $[(CO)_3FeH(SiPh_3)(Me_2PCH_2B(OMe)Cl)]$ (**20**)

A solution of 1.09 g (2.00 mmol) **19** in 50 ml of a hexane/toluene mixture (10:1) was cooled to $-78^\circ C$ and 0.81 ml of a 2.48 M solution of BCl_3 in hexane was added dropwise. The mixture was warmed to room temperature, concentrated to 25 ml and cooled to $-30^\circ C$. The product was isolated as a white solid. Yield: 0.87 g (78.7%). 1H NMR: δ -9.55 (d, $^2J_{PH} = 29.90$ Hz, 1H, FeH), 0.95 (d, $^2J_{PH} = 8.83$ Hz, 6H, PCH_3), 1.12 (d, $^2J_{PH} = 9.05$ Hz, 2H, PCH_2B), 3.28 (s, 3H, $BOCH_3$), 7.15 (br, 9H, *o*- and *p*-H $SiPh_3$), 7.88 (br, 6H, *m*-H $SiPh_3$). ^{11}B NMR: δ_B 38.87. ^{13}C NMR: δ 21.00 (d, $^1J_{PC} = 27.5$ Hz, PCH_3), 21.40 (br, PCH_2B), 54.90 (s, OCH_3), 136.30 (br, *o*-, *m*-, *p*-C $SiPh_3$), 143.00 (s, *ipso*-C $SiPh_3$), 212.12 (d, $^2J_{PC} = 20.3$ Hz, FeCO). $^{31}P\{^1H\}$ NMR: δ_P 19.19. IR: ν_{CO} 2036(w), 1977(m), 1960(s). MS: m/z (relative intensity) = 259 (40%, $SiPh_3^+$), 232 (10%, $M^+-CO-Cl-SiPh_3$), 204 (11%, $M^+-2CO-Cl-SiPh_3$), 182 (100%, $SiPh_2$). Anal. Calcd. for $C_{25}H_{27}BO_4SiPClFe$ (552.66): C, 54.33; H, 4.92. Found: C, 53.91; H, 4.93.

2.16. Structure determination of **19**

A white crystal of approx. dimensions $0.70 \times 0.55 \times 0.50$ mm was studied on an ENRAF-NONIUS CAD4 diffractometer with graphite-monochromized Mo K α

Table 1
Summary of X-ray crystallographic data for **19**

Empirical formula	$FePSiO_5C_{26}BH_{30}$
Fw	548.24
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
a (\AA)	11.254(5)
b (\AA)	11.240(3)
c (\AA)	12.426(3)
α ($^\circ$)	86.53(2)
β ($^\circ$)	85.20(3)
γ ($^\circ$)	61.71(3)
V (\AA^3)	1378.8(8)
d_{calcd} (g cm^{-3})	1.320
Z	2
$F(000)$	572
μ (Mo K α) (cm^{-1})	6.8
T (K)	203
Scan mode	ω -2 θ
Scan range ($^\circ$)	$3 \leq \theta \leq 25$
Total no. of data	7933
No. of unique observed	4262
Data $I > 1.0\sigma(I)$	
No. of variables	436
R, R_w	0.028, 0.035
Weighting factor, w	$w = 1/\sigma^2(F_o)$
GO F	1.243
Max. resid. density ($e \text{\AA}^{-3}$)	0.34

radiation ($\lambda = 0.71073 \text{\AA}$). Crystal data and parameters of data collection and structure refinement are compiled in Table 1. The structure was solved by the Patterson method and the remaining atom positions resulted from subsequent cycles of refinement and difference fourier syntheses [28]. In the final least-squares full-matrix refinement, all non-hydrogen atoms were refined with anisotropic thermal displacement parameters, and hydrogen atoms with isotropic displacement parameters. An empirical absorption correction was applied (ψ scans) [29].

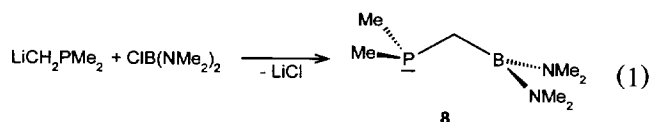
3. Results and discussion

3.1. Synthesis and reactions of the free ligand

We chose $Me_2PCH_2B(NMe_2)_2$ (**8**) as a first model ligand for our investigations for several reasons: (i) this compound is readily available, (ii) the NMe_2 -groups at boron should prevent the molecule from dimerization, and (iii) several methods are known to substitute the NMe_2 -groups by more reactive ligands.

Reaction of Me_2PCH_2Li with $CIB(NMe_2)_2$ in THF at low temperatures gave the product **8** as a colorless air-sensitive liquid in high yield. The ^{31}P NMR signal at $\delta = -48.8$ ppm is shifted downfield by 13 ppm in comparison with PMe_3 [30] which is in accordance with the electron withdrawing character of the neighbouring boron atom. This shift and the ^{11}B NMR signal at 31.05

ppm clearly indicate a coordination number of three for each of these atoms, thus, excluding any bonding interactions between phosphorus and boron as to be expected due to π -backbonding from the nitrogen atoms to the boron center.



We investigated exchange reactions of the NMe_2 -substituents of **8** in order to generate a variety of such ligands, but in contrast to the behavior of known alkyl(diamino)boranes, all attempts to introduce methoxy or chlorine substituents at the boron atom of **8** by reactions with MeOH , BCl_3 or HCl , respectively, led to mixtures of several species which exhibited high field shifted ^{11}B NMR signals in the characteristic region of fourfold coordinated boron between 7.15 and -17.17 ppm showing no splitting or broadening due to boron–phosphorus interactions. A possible decomposition of the expected derivatives of **8** is not very likely, since recently, we obtained very similar compounds of the type $o\text{-Ph}_2\text{PC}_6\text{H}_4\text{CH}_2\text{BX}_2$ ($\text{X} = \text{NMe}_2, \text{OMe}, \text{Cl}, \text{H}$) [31], which proved to be very stable under these conditions.

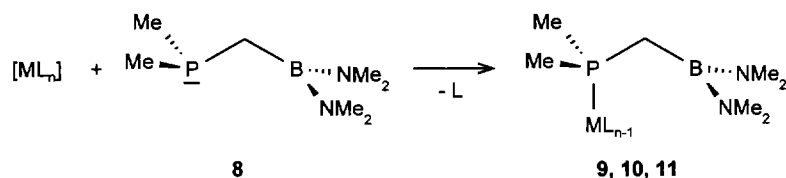
3.2. Synthesis of the phosphane complexes

The transition metal phosphane complexes **9**, **10**, and **11** were obtained by reactions of $[(\text{CO})_5\text{Cr}(\text{THF})]$, $[(\text{MeC}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{THF})]$, and $[\text{Fe}_2(\text{CO})_9]$, respectively, with **8** at room temperature and isolated by distillation as yellow or colorless oils in yields between 70 and 88% (Eq. (2)). The chromium and manganese THF complexes were generated in situ by irradiation of the corresponding carbonyl compounds in THF [24,25]. The composition of compounds **9**, **10**, and **11** is proved by elemental analyses and mass spectra. Their structure in solution could be deduced unambiguously from their NMR and IR spectra. The complexes show in solution ^{11}B NMR signals in the range of 31.03 to 32.67 ppm,

Table 2
 ^{11}B NMR, ^{31}P NMR, and IR data

Compound	$\delta^{11}\text{B}$ (ppm)	$\delta^{31}\text{P}$ (ppm)	ν_{CO} (cm^{-1})
8	31.05	-48.80	–
9	32.67	16.81	2060, 1976, 1931
10	31.03	57.18	1919, 1845
11	31.50	44.16	2046, 1968, 1931
12	29.20	12.45	2059, 1974, 1931
13	28.00	44.16	2046, 1968, 1931
14	35.12	41.28	2045, 1967, 1930
15	7.17	36.23	2045, 1965, 1927
16	-33.86	43.37	2031, 1950, 1918
17	20.46	40.42; 40.59 (70:30)	2048, 1973, 1935
18	-13.60	42.11	2040, 1962, 1923
19	28.70	18.97	2035, 1980, 1963
20	31.50	44.16	2046, 1968, 1931

thus, being almost unchanged with respect to the free ligand **8**. Compounds **9**, **10**, and **11** exhibit ^{31}P NMR signals of 16.81, 57.18, and 44.16 ppm, respectively. The comparison with trialkylphosphanes coordinated to $(\text{CO})_5\text{Cr}$, $\text{CpMn}(\text{CO})_2$, and $(\text{CO})_4\text{Fe}$ moieties [32–34] reveals, that the slight downfield shift of the ^{31}P NMR signal of the free ligand obtains also for the metal-bound $\text{Me}_2\text{PCH}_2\text{B}(\text{NMe}_2)_2$. The transition metal centers themselves, however, are not affected as shown by the IR data (Table 2) which show no significant difference in comparison to the corresponding PMe_3 derivatives [32,34,35]. Compound **9** shows in solution three IR bands in the carbonyl region as to be expected for an octahedral $[\text{M}(\text{CO})_5\text{L}]$ complex [36]. In the ^{13}C NMR spectrum, two doublets due to a $^2J_{\text{PC}}$ coupling in a 4:1 ratio for the equatorial and the axial CO ligands are present. The IR and NMR spectra of **10** also meet the expectations, showing two CO bands in the IR and one doublet in the ^{13}C NMR spectrum for the equivalent CO ligands. The phosphane ligand in compound **11** adopts an axial position as shown by three IR bands. On the NMR time scale, however, we find a fast exchange between equatorial and axial positions, due to Berry pseudo-rotation which is often documented for trigonal bipyramidal complexes, resulting in one doublet for the carbon atoms of the CO ligands in the ^{13}C NMR spectrum [36].



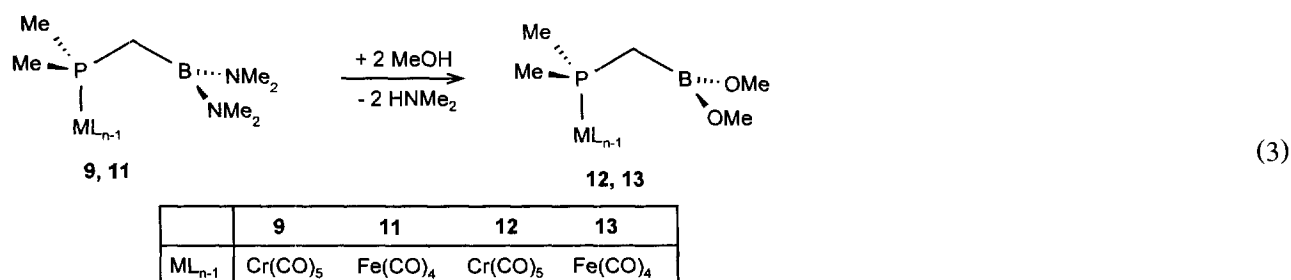
	9	10	11
ML_{n-1}	$\text{Cr}(\text{CO})_5$	$(\text{MeC}_5\text{H}_4)\text{Mn}(\text{CO})_2$	$\text{Fe}(\text{CO})_4$

3.3. Reactions of the metal coordinated ligand

In contrast to the failed exchange reactions of the Me₂N substituents of free Me₂PCH₂B(NMe₂)₂ (**8**), the metal coordinated phosphane, however, underwent cleanly various substitution reactions, and ligands such as H, Cl, and MeO were introduced at boron. These substituents affect the ¹¹B NMR shifts of the new compounds, but show no influence on other spectroscopical data (Table 1); especially IR and ³¹P NMR

data are in the usual range for complexes of the type [(R₃P)M(CO)_n] (M = Cr, n = 5; M = Fe, n = 4) [32,34,35].

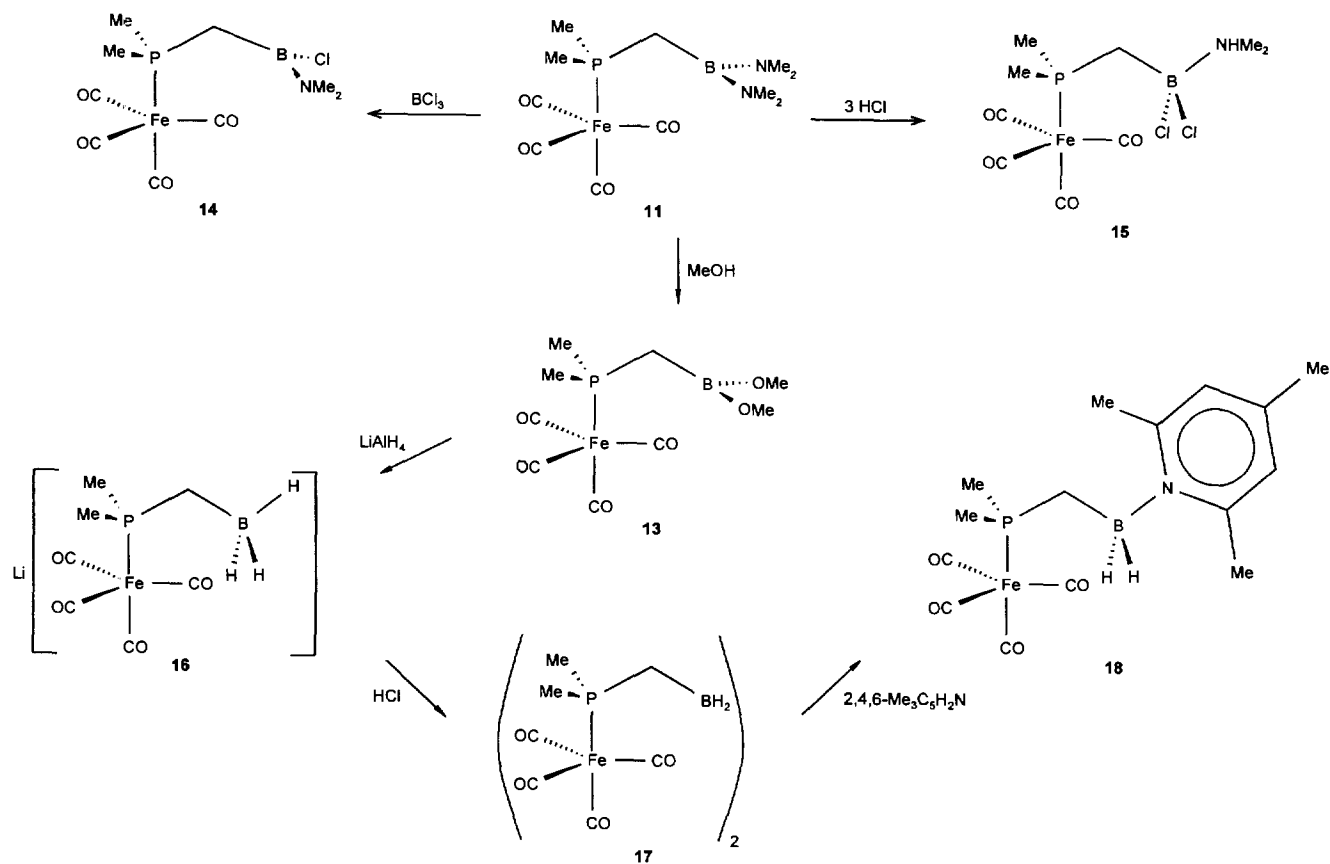
The reactions of **9** and **11** with an excess of MeOH gave [(CO)₅Cr{Me₂PCH₂B(OMe)₂}] (**12**), and [(CO)₄Fe{Me₂PCH₂B(OMe)₂}] (**13**), respectively, which were isolated as high volatile liquids in yields > 70% (Eq. (3)). The methoxy groups at boron cause slight high field shifts of the ¹¹B NMR signals of about 3 ppm with respect to the starting compounds.



The introduction of chlorine at the boron atom of **11** was achieved by either treatment with one equivalent of BCl₃, or by addition of an excess of HCl (Eq. (4)). The first reaction led to substitution of one dimethylamino group giving [(CO)₄Fe{Me₂PCH₂B(NMe₂)Cl}] (**14**) as a yellow solid. An excess of HCl, however, gave the dichloroborane compound, which added the free HNMe₂ under formation of white, solid [(CO)₄Fe{Me₂PCH₂BCl₂-(HNMe₂)}] (**15**). These compounds show characteristic ¹¹B NMR signals for tri- and tetrafold coordinated boron atoms, respectively, at δ = 35.12 and δ = 7.17. Both products show significant decomposition in solution at room temperature after thirty minutes.

The diborane(6) derivative [(CO)₄Fe{Me₂PCH₂BH₂}]₂ (**17**) was obtained in a two step reaction from [(CO)₄Fe{Me₂PCH₂B(OMe)₂}] (**13**) by treatment with Li[AlH₄] and HCl, subsequently (Eq. (4)). Li[AlH₄] converts **13** into the corresponding lithium borate Li[(CO)₄Fe{Me₂PCH₂BH₃}] (**16**), which was isolated as a white solid and characterized by NMR methods. Reaction of the isolated lithium salt with one equivalent HCl, being added as a solution in diethylether at -78°C, gave the diborane(6) **17**. The isolated compound shows to sets of signals in a ratio of 70:30 in ¹H, ¹³C, and ³¹P

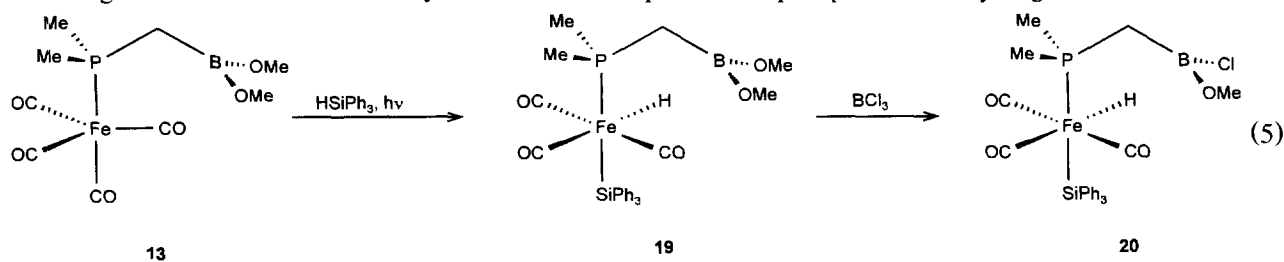
NMR spectra, which are temperature independent up to 90°C. This double set of signals is due to a *cis*, *trans*-position of the -{CH₂P(Me₂)}Fe(CO)₄ moieties with respect to the central B₂H₄ unit [37]. A characteristic ¹¹B NMR shift at δ = 20.46 is found for this diborane(6) derivative. The presence of bridging and terminal hydrogen atoms can be deduced from ¹H NMR and IR spectra. NMR signals in the region of δ = 0.5 and δ = 4.0 as well as IR bands at 2586 cm⁻¹ and 1605 cm⁻¹ are to be expected for the terminal and bridging hydrogen atoms, respectively [38]. A 2D-¹H-¹¹B-HMQC experiment shows crosspeaks between the signals of both kinds of hydrogen atoms of each isomer and the ¹¹B NMR resonance, thus, giving another evidence for the existence of the B₂H₄ unit in solution. On the addition of collidine (collidine = 2,4,6-Me₃C₅H₂N) the hydrogen bridges were cleaved, and the corresponding borane adduct [(CO)₄Fe{Me₂PCH₂BH₂(2,4,6-Me₃C₅H₂N)}] (**18**) was formed. The compound was isolated as a white solid almost quantitatively. It shows a high field shifted ¹¹B NMR signal at δ = -13.60 and a doublet of triplets for the boron bound hydrogen atoms in the ¹H{¹¹B} NMR spectrum due to a ³J coupling to phosphorus and a ³J coupling to the protons of the methylene unit between boron and phosphorus.



Irradiation experiments were carried out with the diborane(6) derivative $[(\text{CO})_4\text{Fe}(\text{Me}_2\text{PCH}_2\text{BH}_2)_2]$ (**17**) and the corresponding collidine adduct $[(\text{CO})_4\text{Fe}(\text{Me}_2\text{PCH}_2\text{BH}_2(2,4,6\text{-Me}_3\text{C}_5\text{H}_2\text{N}))]$ (**18**), respectively, to examine, if these compounds undergo an oxidative addition of the boron–hydrogen bond to the iron center under displacement of a CO-ligand. All these experiments, however, which were carried out in inert solvents like hexane at temperatures between -30°C and 20°C led to decomposition of the starting materials within few minutes. It was not possible to characterize any products by multinuclear NMR or IR methods from the reaction mixtures.

3.4. Addition of HSiPh_3 to the iron center

Since the irradiation experiments with compounds **17** and **18** gave no satisfactory results,



$[(\text{CO})_4\text{Fe}(\text{Me}_2\text{PCH}_2\text{B}(\text{OMe})_2)]$ (**13**) was reacted with HSiPh_3 under similar conditions to check, if phosphane complexes of the type $[(\text{CO})_4\text{Fe}(\text{Me}_2\text{PCH}_2\text{BX}_2)]$ are available for oxidative additions of suitable element–hydrogen bonds at all. A silane was chosen for this reaction, because various examples for the photochemically induced formation of iron-silyl complexes are known [39], and due to the diagonal relationship, the chemistry of boron and silicon show many similarities.

Irradiation of **13** in the presence of HSiPh_3 led under elimination of CO to $[(\text{CO})_3\text{FeH}(\text{SiPh}_3)(\text{Me}_2\text{PCH}_2\text{B}(\text{OMe})_2)]$ (**19**) (Eq. (5)), which was obtained as a white crystalline product in 95% yield. The ^{31}P NMR signal at $\delta = 19.97$, the characteristic $^2J_{\text{PH}}$ coupling constant of 29.74 Hz and the ν_{CO} bands in the IR spectrum at 2035(w), 1980(s), and 1963(vs) cm^{-1} compare to the data of corresponding complexes of the type *mer*- $[(\text{CO})_3\text{FeH}(\text{SiR}_3)(\text{PR}_3)]$, showing a *cis* position of phosphorus and hydrogen [39].

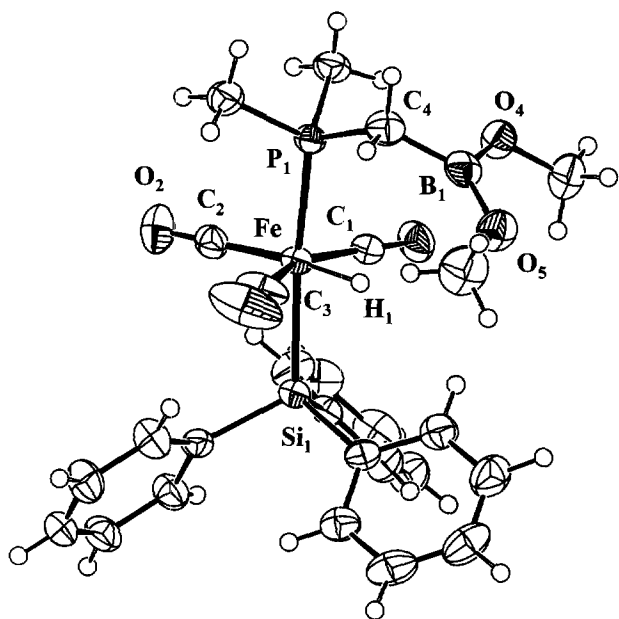


Fig. 2. Platon plot of **19**; ellipsoids with 50% probability.

The X-ray structure determination of **19** reveals that the compound adopts a *mer*-geometry also in the crystal (Fig. 2). The complex shows a distorted octahedral coordinated iron center with a P–Fe–Si angle of 172.96(2)° (Table 3). The Fe–P and Fe–Si distances are 2.2299(5) Å and 2.3600(5) Å, respectively. The boron atom is trigonal planar coordinated with B–O distances of about 1.35 Å and the phosphorus atom exhibits a distorted tetrahedral coordination. Reaction of **19** with one equivalent BCl₃ led to exchange of one boron bound methoxy group (Eq. (5)) under formation of [(Ph₃Si)(CO)₃HFe(Me₂PCH₂B(OMe)Cl)] (**20**) which was isolated in 80% yield as a white crystalline product. The compound shows a characteristic low field shift of the ¹¹B NMR signal to δ = 38.87; all other spectroscopical data, however, show no significant change.

Table 3
Selected bond distances (Å) and angles (°) for **19**

Distances (Å)		Angles (°)	
Fe–P	2.2299(5)	P–Fe–Si	172.96(2)
Fe–Si	2.3600(5)	P–Fe–C1	93.52(6)
Fe–H1	1.33(3)	P–Fe–H1	91(1)
Fe–C1	1.769(2)	Si–Fe–H1	82(1)
Fe–C2	1.788(2)	Si–Fe–C1	86.84(6)
Fe–C3	1.766(2)	Fe–P–C4	114.04(7)
P–C4	1.822(2)	Fe–P–C5	115.23(7)
B–C4	1.577(3)	C4–B–O4	125.2(2)
B–O4	1.351(3)	C4–B–O5	116.6(2)
B–O5	1.356(3)	O4–B–O5	118.2(2)

4. Conclusions

We reported the synthesis of α,ω -[phosphanly(organyl)]borane Me₂PCH₂B(NMe₂)₂ (**8**) and its reactions with various transition metal complexes, giving the new compounds [(CO)₅Cr{Me₂PCH₂B(NMe₂)₂}] (**9**), [(MeC₅H₄)Mn(CO)₂{Me₂PCH₂B(NMe₂)₂}] (**10**) and [(CO)₄Fe{Me₂PCH₂B(NMe₂)₂}] (**11**). In contrast to the uncoordinated Me₂PCH₂B(NMe₂)₂, the Me₂N groups of **11** were exchanged by methoxy, chlorine, and hydrogen substituents, respectively, thus, providing a number of reactive groups at boron. Besides, the oxidative addition of HSiPh₃ to the iron center of [(CO)₄Fe{Me₂PCH₂B(OMe)₂}] (**13**) gave compounds like [(CO)₃FeH(SiPh₃){Me₂PCH₂B(OMe)₂}] (**19**).

Even if the intramolecular formation of a boron–metal bond was not achieved yet, these results demonstrate the possibility of (1) introducing an α,ω -[phosphanly(organyl)]borane as a phosphorus bound ligand to transition metals and (2) substitution of both the ligands at boron and the metal center. Especially the photochemically induced synthesis of **19** in almost quantitative yields shows, that further investigations with ligands of the type R₂P(CR_m)_nBX₂ (R = alkyl or aryl; m = 1, 2; n ≥ 1; X = H, NR₂; OR) are worth to be pursued. In particular, similar ligands with two or three carbon atoms between phosphorus and boron are subject of our further studies.

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